

Pietropaolo *et al* Reply: The harmonic model in Ref. [1] has been previously applied to the cases of H₂S [2] and water [3]. It is assumed that proton dynamics along two orthogonal directions in the plane of the molecule are equivalent, with Gaussian momentum distribution (GMD) both in and out of the molecular plane. This is equivalent to assuming GMD both along the direction of the hydrogen bond and perpendicular to it. The three-dimensional momentum distribution, when spherically averaged, can be represented as [4]

$$n(p) = \left\langle \frac{1}{\sqrt{8\pi^3\sigma_z^2\sigma_t^2}} \exp^{-\frac{1}{2}\left[\left(\frac{p_z^2}{\sigma_z^2} + \frac{p_t^2}{\sigma_t^2}\right)\right]} \right\rangle_{\Omega} \\ = \frac{e^{-(p^2/2\sigma^2)}}{(\sqrt{2\pi}\sigma)^3} \left[1 + \sum_{n \geq 2} c_n (-1)^n L_n^{\frac{1}{2}}\left(\frac{p^2}{2\sigma^2}\right) \right], \quad (1)$$

where $L_n^{\frac{1}{2}}$ are generalized Laguerre polynomials, $\sigma^2 = \frac{2\sigma_z^2 + \sigma_t^2}{3}$, where σ_z^2 , σ_t^2 are the variances of the GMD along and perpendicular to the hydrogen bond, respectively, and $c_n = \frac{(\sigma_t^2 - \sigma_z^2)^n}{\sigma^2} \langle (1/3 - \cos^2\theta)^n \rangle_{\Omega}$. It has been shown that $\sigma_z \sim 2\sigma_t$ and $n(p)$ is determined mainly by the motion in the OH stretch direction [3,5]. Large changes of σ_z and

$n(p)$ between 300 and 269 K are not expected, given the temperature evolution of the stretching band [6]. If we fit our data [7] according to Eq. (1), the c_n values give an unjustified $\sigma_z \sim 1.1\sigma_t$. Indeed the right-hand side of Eq. (1), with arbitrary c_n coefficients, allows to take into account both spherically averaged GMD, and non-Gaussian components resulting from anharmonicities and nodes in $n(p)$ [8]. In the best fit of our data only c_2 is significant and its value is a consequence of a flat-bottomed [9] or double-well potential [10], with the associated delocalization. In Fig. 1 we show that the longitudinal $n(p)$ at $T = 271$ K [7] cannot be fitted by a spherically averaged GMD, at odds with liquid water at room temperature or approaching the supercritical phase [3,11]. A visual inspection of the experimental longitudinal $n(p)$ at $T = 271$ K shows a width about 10% larger than the width at $T = 269$ K (see Fig. 1 of Ref. [7]). Consequently, a change of at least 10% in the mean kinetic energy, $\langle E_k \rangle_H$, is expected, regardless of the model line shape employed. The secondary structures in the radial $n(p)$ at 271 K suggest delocalization along the O-O direction [8–10]. The latter is not necessarily associated with a reduced $\langle E_k \rangle_H$, as expected according to a bare application of the Heisenberg principle. Indeed delocalization and increased $\langle E_k \rangle_H$ can be both observed for a proton in a double-well potential if each well becomes narrower with lowering the temperature, and the energy barrier becomes smaller [10]. On the other hand, delocalization and reduced $\langle E_k \rangle_H$ can also be observed [9].

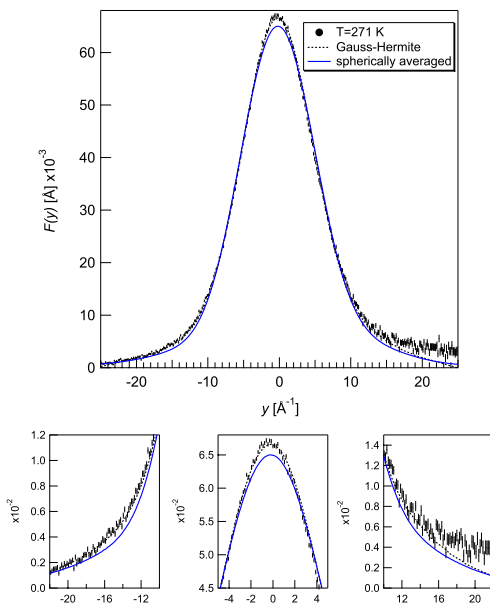


FIG. 1 (color online). Main panel. Experimental detector-averaged longitudinal $n(p)$ in bulk water at $T = 271$ K (points with error bars) and corresponding best fit with arbitrary c_n coefficients [7] (dashed line). Best fit employing the spherically averaged multivariate Gaussian is also shown (solid line). Bottom panels. Same as main panel, showing an enlarged view of the left and right tails, along with the peak region. It can be noticed that Eq. (1) with arbitrary c_n coefficients best fits the experimental data, especially in the range $-22 \text{ \AA}^{-1} \leq y \leq -10 \text{ \AA}^{-1}$ (left bottom panel), in the range $-4 \text{ \AA}^{-1} \leq y \leq 4 \text{ \AA}^{-1}$ (middle bottom panel), and in the range $10 \text{ \AA}^{-1} \leq y \leq 22 \text{ \AA}^{-1}$ (right bottom panel). Note: data at 271 K are reported in red, and those at 269 K in black, contrarily to what is stated in the caption of Fig. 1 [7].

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